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(54) A glazing panel having solar screening properties

(57) A glazing panel having beneficial anti-solar properties for use in vehicle glazing, and in particular in vehicle roof windows, comprises a vitreous substrate carrying a spray-formed pyrolytic tin/antimony oxide coating layer having a thickness of at least 400 nm and containing tin and antimony in a Sb/Sn molar ratio of from 0.05 to 0.5, whereby the coated substrate has a luminous transmittance (TL) of less than 35% and a selectivity (TL/TE) of at least 1.3.

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1350 PHENIX

A GLAZING PANEL HAVING SOLAR SCREENING PROPERTIES

The present invention relates to a glazing panel having solar screening properties. The panel according to the invention
5 takes the form of a substrate carrying a spray-formed pyrolytic coating containing tin and antimony.

Reflective transparent solar control glazing has become much used in vehicle windows, where the objective is to protect the
10 vehicle occupants against solar radiation. It has been used in railway carriages as side windows and in road vehicles for side, rear and roof windows. It has further been proposed to form the whole roof area of a motor car. It serves to provide protection
15 against solar radiation by reflection and/or absorption and by eliminating the dazzling effects of intense sunshine, thereby giving an effective screen against glare, enhancing visual comfort and reducing eye fatigue.

The properties of the coated substrate discussed herein are
20 based on the standard definitions of the International Commission on Illumination - *Commission Internationale de l'Eclairage* ("CIE").

The standard illuminants quoted herein are CIE Illuminant C and
25 Illuminant A. Illuminant C (mostly used for evaluating the optical properties of glazing panels for buildings) represents average daylight having a colour temperature of 6700°K. Illuminant A (which equates to the light emitted by car headlamps and is therefore generally used to evaluate the

optical properties of glazing panels for motor vehicles) represents the radiation of a Planck radiator at a temperature of about 2856°K.

5 The "luminous transmittance" (TL) is the luminous flux transmitted through a substrate as a percentage of the incident luminous flux.

10 The "luminous reflectance" (RL) is the luminous flux reflected from a substrate as a percentage of the incident luminous flux.

The "energy transmission" (TE) is the total radiant energy directly transmitted through a substrate as a percentage of the incident radiant energy.

15 The "energy reflection" (RE) is the radiant energy reflected from a substrate as a percentage of the incident radiant energy.

20 The "solar factor" (FS) is the ratio of the sum of the total energy directly transmitted through a substrate (TE) and the energy which is absorbed and re-radiated on the side away from the energy source (AE) as a proportion of the total radiant energy incident on the substrate.

25 The "selectivity" of the coated substrate relates to the balance between luminous transmission and energy transmission. In the case of building glass it is often defined as the ratio of the luminous transmittance to the solar factor (TL/FS), but for

vehicle glass it commonly refers to the ratio of the luminous transmittance to the energy transmission (TL/TE).

5 The "dominant wavelength" (λ_D) is the peak wavelength in the range transmitted or reflected by the coated substrate.

10 The "purity" (p) of the colour of the substrate refers to the excitation purity measured with Illuminant C. It is specified according to a linear scale on which a defined white light source has a purity of zero and the pure colour has a purity of 100%. The purity of the coated substrate is measured from the side opposite the coated side.

15 The "emissivity" (ϵ) is the ratio of the energy emitted by a given surface at a given temperature to that of a perfect emitter (black body with emissivity of 1.0) at the same temperature.

20 From a technical point of view, it is desired that in sunny conditions the glazing shall not pass too great a proportion of total incident solar radiation in order that the interior of the vehicle or building shall not become overheated. The transmission of total incident solar radiation may be expressed in terms of the "solar factor" (defined above). In the case of
25 vehicles the main energy factor to be considered is the total energy directly transmitted (TE), since the energy which is internally absorbed and re-radiated (AE) is dissipated by the movement of the vehicle.

Our earlier patent GB 2200139 describes and claims a method of forming a pyrolytic tin oxide coating on a hot glass substrate by spraying a solution containing a tin compound and additives which produce in the coating both fluorine and such materials as antimony, arsenic, vanadium, cobalt, zinc, cadmium, tungsten, tellurium and manganese so as to give the coating a low emissivity and a low specific internal haze factor. While the resultant coating has many desirable properties it falls short of the combination of properties now being sought for solar-resistant vehicle window glass.

It is an object of the present invention to provide a glazing panel having a high level of solar screening properties in combination with other desirable properties of luminous transmission and high selectivity.

We have discovered that this and other useful objectives can be achieved by a vitreous substrate bearing a thick pyrolytically sprayed coating comprising tin and antimony oxides in a specific relative ratio.

Thus, according to the present invention, there is provided a glazing panel comprising a vitreous substrate carrying a spray-formed pyrolytic tin/antimony oxide coating layer having a thickness of at least 400 nm and containing tin and antimony in a Sb/Sn molar ratio of from 0.05 to 0.5, whereby the coated substrate has a luminous transmittance (TL) of less than 35% and a selectivity (TL/TE) of at least 1.3.

A number of techniques are known for forming coatings on a vitreous substrate, including pyrolysis and cathode sputtering. Pyrolysis generally has the advantage of producing a hard coating, which precludes the need for a protective layer. The coatings formed by pyrolysis have durable abrasive- and corrosion-resistant properties. It is believed that this is due in particular to the fact the process involves depositing of coating material onto a substrate which is hot. Pyrolysis is also generally cheaper than alternative coating processes such as sputtering, particularly in terms of the investment in plant.

The substrate is preferably in the form of a ribbon or sheet of vitreous material, such as glass or some other transparent rigid material. In view of the proportion of incident solar radiation which is absorbed by the glazing panel, especially in environments where the panel is exposed to strong or long-term solar radiation, there is a heating effect on the panel which may require that the substrate be subsequently subjected to a toughening process. However, the durability of the coating enables the panel to be mounted with the coated face outermost, thus reducing the heating effect.

Preferably the substrate is formed of coloured glass. It is found that the combination of coloration within the material of the glass and a coating according to the invention facilitates the achievement of the required low luminous transmission and high selectivity. The generally preferred colours for glass used in vehicle roofs, side or rear windows are grey and green.

The tin/antimony oxide coating preferably has a thickness of from 400 to 800 nm, most preferably 450 to 700 nm. Such thicknesses permit the achievement of a low total transmitted energy factor (TE) while retaining a sufficient level of light transmission. Thick layers of tin/antimony oxide, particularly layers having a low Sb/Sn molar ratio, can not only provide a glazing panel with the required low luminous transmission and high selectivity but also with the advantageous combination of a low solar factor FS and low emissivity.

It may be useful to prevent interaction between the glass of the substrate and the tin/antimony oxide coating layer. As an example, it has been found that in the pyrolytic formation of a tin oxide coating from tin chloride on a soda-lime glass substrate, sodium chloride tends to become incorporated into the coating as a result of reaction of the glass with the coating precursor material or its reaction products, and this leads to haze in the coating. Thus, an intermediate haze-reducing coating layer may if desired be positioned between the substrate and the tin/antimony oxide coating layer. Such an intermediate layer is generally unnecessary for low luminous transmission panels since the haze is not noticeable to any significant extent. If used it may comprise a silicon oxide having a geometric thickness such as about 100 nm. The presence of a silicon oxide undercoating on soda-lime glass has the benefit of inhibiting the migration of sodium ions from the glass whether by diffusion or otherwise into the tin/antimony oxide coating layer either during formation of that upper layer or during a subsequent high temperature treatment.

Panels according to the invention are particularly well suited to use as vehicle roof panels, for example to tilting or sliding sunroofs, or even to form substantially the whole of the vehicle roof area. They may also advantageously be used as vehicle rear or rear side windows.

Glazing with a luminous transmittance of less than 35 % is advantageous as a vehicle roof panel, most particularly if the panel is to form most or all of the roof area. While such a low level of luminous transmission is required according to the invention, it is also desirable that the glazing panel shall transmit some visible light in order to give a contribution to the natural illumination of the interior of the vehicle.

A high level of selectivity of the coating in combination with a low level of luminous transmission allows a low solar energy transmission. The selectivity provided by the invention is essentially at least 1.3 and preferably at least 1.5. It is a particular benefit of the invention that in practice it permits the achievement of selectivity values close to 2.

The energy transmission (TE) is therefore preferably less than 15%, most preferably less than 10%. Such low energy transmission assists in reducing the load on a vehicle air conditioning system.

For a whole-roof panel it may be advantageous to employ a panel with a luminous transmittance as low as 10% and energy

transmission of just 5%, giving a selectivity of 2. For an opening roof panel somewhat higher transmission is generally preferred, for example luminous transmittance of about 20% and energy transmission of about 12 %, again giving a selectivity approaching 2.

The Sb/Sn molar ratio in the coating is preferably in the range 0.07 to 0.20, most preferably 0.08 to 0.15. The preferred ranges arise from the need to have sufficient antimony to be effective in giving the required low transmission properties while not being present in sufficient amounts to affect the optical quality.

Conveniently the coating comprises simply a single layer of tin/antimony oxide. However, it is possible to provide one or more further coating layers, whether applied by pyrolysis or by other coating methods, to achieve certain desired optical qualities. It should be noted however, that the tin/antimony oxide layer when applied by pyrolysis has sufficient mechanical durability and chemical resistance to suitably serve as the exposed layer. Alternatively the said layer can be applied to the surface of the substrate that is to face the interior of a vehicle.

The panels according to the invention have properties of low reflectivity of visible light which are particularly advantageous for vehicle glazing. Preferably the reflectivity of visible light (RL) is lower than 12%, and may typically be between 5 and 12%.

The panels according to the invention may be installed in single or multi-glazed assemblies. The coating layers are applied to the hot substrate by spraying reactants in a liquid state, for example by means of a spray nozzle. While liquid spraying lacks the precision of alternative pyrolytic method of chemical vapour deposition (CVD), it is a convenient and inexpensive method for deposition of a thick coating layer, as in the present case. Indeed CVD is generally not a convenient method for the formation of thick coatings.

Especially in the preferred instance of applying the coating to a coloured substrate any variations, resulting from the use of a spray method, in thickness or uniformity of the coating are barely visible. Preferably the source of tin is SnCl_2 and the source of antimony is SbCl_3 , both materials being added to water for the spraying operation. Dissolved organometallic material may also be used.

When it is desired to manufacture pyrolytically coated flat glass, it is best to do so when the glass is newly formed. To do so has economic benefits in that there is no need to reheat the glass for the pyrolytic reactions to take place, and it also has benefits as to the quality of the coating, since it is assured that the surface of the glass is in pristine condition. Preferably, therefore, said coating precursor material is brought into contact with an upper face of a hot glass substrate constituted by freshly-formed flat glass.

Thus, the glazing panels according to the invention may be manufactured as follows. The pyrolytic coating step may be carried out at a temperature of at least 400°C, ideally from 550°C to 750°C.

5

To form each coating, the substrate is brought into contact, in a coating chamber, with a spray of droplets containing the antimony- and tin-containing reactants. The spray is applied by one or more spray nozzles arranged to follow a path which provides the coating across the width of the ribbon to be coated.

10

In a spray-pyrolysis method the Sb/Sn molar ratio in the finished coating is not directly proportional to the ratio in the reactant mixture, and indeed is usually substantially different therefrom. The level of incorporation of antimony into the coating is significantly affected by such parameters as the spray rate, the type of glass and the glass temperature. Attempts to compute the coating proportions from the starting proportions are therefore unreliable and it is usually necessary to undertake preliminary trials to determine the starting proportions to meet the required coating proportions in a specific instance.

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Following deposition the coatings are preferably polished, using any desired conventional polishing means. The coated product may also if desired be subjected to tempering.

The invention will now be described in more detail with reference to the following non-limiting examples.

5 In the Examples the Sb/Sn molar ratio in the coating layers was determined by an X-ray analysis technique in which the number of X-ray counts of the respective elements was compared. While this technique is not as precise as if a calibration by chemical dosage were made, the similarity of antimony and tin means that they respond similarly to X-rays. The ratio of the measured
10 number of observed counts of the respective elements thus provides a close approximation to their molar ratio.

EXAMPLES 1-21

15 In all the examples a Sb/Sn mixture was applied in an aqueous mixture to a moving ribbon of hot glass substrate having a thickness of 4 mm. Several different types of glass were employed, as shown in Table A below. The initials in the headings to this and the other following tables (TL, TE etc.)
20 have the meanings described above. The columns FS p1 and FS p2 in Table C refer to the solar factor at, respectively, the side of the glass facing the light source (position 1) and the side remote from the light source (position 2). Unless otherwise indicated the properties shown in the tables were measured under
25 illuminant C. Under the conditions described the difference in TL between using illuminant C and illuminant A (more generally used in the field of automobile vehicles) was minimal, being of the same order of magnitude as routine errors of measurement.

In each case the mixture was a coating precursor solution containing approximately 1000g (in total) of SnCl_2 and SbCl_3 per litre of the mixture and in the proportions shown in Table B below. The solution was applied to the substrate by a reciprocating spray nozzle which followed a path across the width of the ribbon.

Table A

<u>Glass Type</u>	Clear	Green A	Green C	Grey	Med. Grey 1	Med. Grey 2
λD in transmission (nm) [Illuminant: C/A]		505.4/508.5	509.7/510.2	470.1/493.9	493.2/502.7	494.6/502.8
Purity (%)		2.9/3.4	3.2/4.0	1.5/0.8	5.6/5.1	9.9/9.3
TL (%) [Illuminant: C/A]	89.0	72.66/71.12	67.36/65.69	55.65/55.56	36.8/35.8	37.07/35.13
TE (%) (CIE)	83.0	44.0	37.1	56.9	25.9	20.9
TL/TE (CIE C)	1.07	1.65	1.81	0.98	1.42	1.77
FS p1 (CIE) (%)	86.0	56.8	51.7	66.3	43.4	39.7
TL/FS	1.03	1.28	1.30	0.84	0.85	0.93

The sprayed tin and antimony components reacted to form a pyrolytic tin oxide coating on the glass. The parameters employed and the results obtained are shown in Tables B and C. It will be noted that Examples 4 and 5 do not satisfy the requirements of the claims herein in respect of the required coating thickness and selectivity and in the case of Example 5 also in respect of the required luminous transmission. These

examples are included for comparison to show how operating outside the scope of the claims produces inferior results.

Table B

Example	Glass Type	Sb/Sn of reactants	Sb/Sn of coating	Coating thickness (nm)	TL (%)	RL (%)
1	Clear	0.20	0.11	535	23.0	10.0
2	Clear	0.20	0.12	470	27.0	10.0
3	Clear	0.30	0.14	670	13.0	10.0
4	Clear	0.30	0.16	306	27.0	11.0
5	Clear	0.30	0.19	119	56.0	10.0
6	Green A	0.30	0.17	670	10.4	9.9
7	Green C	0.30	0.14	670	9.6	9.9
8	Med. Grey 2	0.30	0.14	520	6.4	10.5
9	Med. Grey 2	0.30	0.14	520	6.5	10.5
10	Green A	0.20	0.11	530	15.7	10.3
11	Green C	0.20	0.11	530	17.3	10.3
12	Med. Grey 1	0.20	0.11	530	9.5	10.2
13	Med. Grey 2	0.20	0.11	530	9.6	10.2
14	Grey	0.175	0.11	640	15.0	10.0
15	Grey	0.175	0.11	530	19.0	10.0
16	Green A	0.175	0.11	640	19.0	10.0
17	Green A	0.175	0.11	530	25.0	10.0
18	Green C	0.175	0.11	640	17.8	10.0
19	Green C	0.175	0.11	530	23.0	10.0
20	Med. Grey 1	0.175	0.11	640	10.0	10.0
21	Med. Grey 2	0.175	0.11	530	12.6	10.0

Table C

Example	TE (%)	RE (%)	FS p1 (%)	FS p2 (%)	Emissivity (n)	TL/TE	TL/FS
1	17.0	11.0	35.0	31.0	0.35	1.35	0.66
2	21.0	11.0	38.0	39.0		1.29	0.71
3	10.0	11.0	30.0	26.0		1.30	0.43
4	25.0	13.0	41.0	42.0	0.53	1.08	0.66
5	51.0	13.0	60.0	61.0	0.76	1.14	0.97
6	5.8	10.9	26.8	22.9	0.35	1.80	0.39
7	5.1	10.9	26.3	22.3	0.35	1.90	0.36
8	4.2	10.9	25.6	22.0	0.40	1.52	0.25
9	3.5	10.9	25.1	21.5	0.40	1.86	0.26
10	10.0	11.1	29.9	25.8	0.35	1.87	0.62
11	8.7	11.1	28.9	24.8	0.35	1.99	0.60
12	5.5	11.0	26.6	22.3	0.35	1.73	0.36
13	4.8	11.0	26.0	21.7	0.35	2.00	0.37
14	10.0	11.0	30.0			1.50	0.50
15	14.0	11.0	33.0			1.36	0.58
16	9.8	11.0	29.8			1.94	0.64
17	13.0	11.0	32.0			1.92	0.78
18	8.6	11.0	28.9			2.07	0.62
19	11.0	11.0	31.0			2.09	0.74
20	5.4	11.0	26.5			1.85	0.38
21	7.7	11.0	27.7			1.77	0.45

As variations to Examples 14 and 20, coatings were obtained having a thickness of 730 nm and an Sb/Sn ratio of 0.10. In both cases the resulting properties were substantially the same as the original Examples 14 and 20.

The product coated substrate in all the examples had a blue tint in transmission, with a dominant wavelength (λ_D) between 470 and 490 nm, and a haze value between 0.7 and 1.1.

CLAIMS

1. A glazing panel comprising a vitreous substrate carrying a spray-formed pyrolytic tin/antimony oxide coating layer having a thickness of at least 400 nm and containing tin and antimony in a Sb/Sn molar ratio of from 0.05 to 0.5, whereby the coated substrate has a luminous transmittance (TL) of less than 35% and a selectivity (TL/TE) of at least 1.3.

2. A glazing panel according to claim 1, in which the vitreous substrate is made of coloured glass.

3. A glazing panel according to claim 1 or claim 2, in which the tin/antimony oxide coating has a thickness of from 400 nm to 800 nm.

4. A glazing panel according to any preceding claim, in which the tin/antimony oxide coating has a thickness of from 450 nm to 700 nm.

5. A glazing panel according to any preceding claim, wherein the coated substrate has a selectivity of at least 1.5.

6. A glazing panel according to any preceding claim, wherein the coated substrate has an energy transmission factor (TE) of less than 15%.

7. A glazing panel according to claim 6, wherein the coated substrate has an energy transmission (TE) of less than 10%.

5 8. A glazing panel according to any preceding claim, wherein the Sb/Sn molar ratio is in the range from 0.07 to 0.20.

9. A glazing panel according to claim 8, wherein the Sb/Sn molar ratio is in the range from 0.08 to 0.15.

10 10. A glazing panel according to any preceding claim, wherein the tin/antimony oxide coating is a single layer.

11. A glazing panel according to any preceding claim,
15 wherein said tin/antimony oxide coating is an exposed coating layer.

12. A glazing panel according to any preceding claim, wherein the reflectivity of visible light (RL) is lower than 12%

20 13. A glazing panel according to any preceding claim, for use as a vehicle roof panel



The Patent Office

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Application No: GB 9611251.1
Claims searched: 1-13

Examiner: Peter Beddoe
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Patents Act 1977 Search Report under Section 17

Databases searched:

UK Patent Office collections, including GB, EP, WO & US patent specifications, in:
UK Cl (Ed.O): C7F (FHB,FHD,FHE,FHX)
Int Cl (Ed.6): C03C (17/23,17/245,17/25); C23C 16/40
Other: Online: WPI, CLAIMS

Documents considered to be relevant:

Category	Identity of document and relevant passage	Relevant to claims
X	GB 2078213 A (BFG) see esp ex 4	1,3,4,8-11
X	GB 2044137 A (SOCIETA ITALIANA) see esp page 6 lines 17-29	1,3,4,8-11
X	GB 1517341 (DAY) see esp table 1	1,3,4,8-11
X	GB 866332 (PITTSBURGH) see esp page lines 21-24	1,3,4,8-11
X	US 5382383 (CATALYSTS) see esp col 5 line 52 -col 6 line 30	1,3,4,8-11
X	US 4983261 (ASEA) see esp col 2 lines 44-68	1,3,4,8-11
X	US 4900634 (GLAVERBEL) see esp exs 1,3,4	1,3,4,8-11
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X	WPI Accession no 91-169065/23 & JP 030103341 A(NIPPON) see abstract	1,3,4,8-11

X	Document indicating lack of novelty or inventive step	A	Document indicating technological background and/or state of the art.
Y	Document indicating lack of inventive step if combined with one or more other documents of same category.	P	Document published on or after the declared priority date but before the filing date of this invention.
&	Member of the same patent family	E	Patent document published on or after, but with priority date earlier than, the filing date of this application.



The
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Applicati n No: GB 9611251.1
Claims searched: 1-13

Examiner: Peter Beddoe
Date of search: 25 July 1996

Category	Identity of document and relevant passage	Relevant to claims
X	WPI Accession no 79-69149B/38 & JP 540103414 A (SHIBARU) see abstract	1,3,4,8-11

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&	Member of the same patent family	E	Patent document published on or after, but with priority date earlier than, the filing date of this application.

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